MULTIDIMENSIONAL COLORIMETERIC GRADATION OF KAOLIN

R. A. Platova,[1] A. A. Shmarina,[1] and Z. V. Stafeeva[1]

The boundaries of the region corresponding to kaolin samples from the Zhuravlinyi Log deposit in the MKO $L^*A^*B^*$ colorimetric system are determined. It is shown that a discriminant analysis makes it possible to interpret the color formation processes in kaolin after it has been worked at different temperatures as well as to evaluate the contribution of variables — color coordinates — in the dominant processes in each heat-treatment interval. A procedure is proposed for identifying the latent (hidden) component of the coloring power of iron compounds in the kaolin. Multidimensional gradation of kaolin samples with respect to whiteness and yellowness according to quality categories is performed.

The suitability of kaolin as a basic component of a ceramic mix is determined, on the one hand, by the technological properties of the slip and the ceramic mix and, on the other hand, by the properties of the calcined material, including the coloristic characteristics.

The main factors affecting the color of kaolin are the following:

the total content of iron-containing minerals and iron, bound with organic compounds;

the ratio of the silicate (isomorphic impurities in kaolinite or in the form of structure-forming atoms, for example, in hydromica) and nonsilicate iron, represented by iron minerals, including goethite, hematite, pyrite, and others;

iron minerals, which can be in the form of micro-inclusions of individual grains or films enveloping particles of clay minerals;

the levels of the structural organization of iron-containing minerals: magnetically dilute iron (isomorphic impurities in kaolinite), molecular-cluster (associates, clusters, polymer networks, smaller than 5 nm), superparamagnetic state of iron (5 – 10 nm particles), crystalline state of iron minerals (particles larger than 20 nm).

The coloristic characteristics of a large number (277) of samples of iron minerals have been analyzed in many works. The effect of these characteristics on the color of clay-containing materials [2, 3] and the dependence of the color of kaolin on the heat-treatment conditions has been studied [4].

Iron minerals differ with respect to the color tone (from red hematite to yellow goethite) as well as the brightness (from light-yellow goethite to grey-black iron sulfide). The

color of iron minerals depends on the dimensions of the crystals. As hematite crystals increase in size from 0.1 to 1.0 μm, their color changes from red-yellow to purple-red [1]. The same color change occurs with aggregation of hematite crystals. Substitution of Al for Fe has a positive effect on the brightness of hematite. Hematite crystals become darker as they become smaller. The darkening and reddening of goethite particles intensifies as the needles decrease in length from 0.80 to 0.05 μm [2].

An important coloristic characteristic of iron minerals is their coloring power. Iron minerals fall into the following sequence with respect to the relative coloring power [1]: hematite ≫ feroxygite > ferrihydrite > goethite.

Therefore, iron minerals in kaolin differ not only with respect to color tone (yellow, red) and lightness (black, grey) but also with respect to their relative coloring power. The result is that kaolin samples with the same content of iron oxides can differ substantially with respect to color and, correspondingly, whiteness.

Consequently, it is necessary to monitor the quality of the kaolin with respect to the content of coloring impurities and the coloristic characteristics. Standards regulating the color of kaolins do not exist at the present time. This lacuna raises a number of problems including the following:

for colorimetric communications, different interpretations relative to the color as a criterion of its suitability for the production of porcelain articles at different levels of competitiveness;

for colorimetric gradation, the absence of a numerical parameter which is suitable for classifying kaolins with different composition, since the system for making assessments

---

[1] Russian State Trade and Economics University, Moscow, Russia; Plast-Rifei JSC, Plast, Chelyabinsk oblast', Russia.
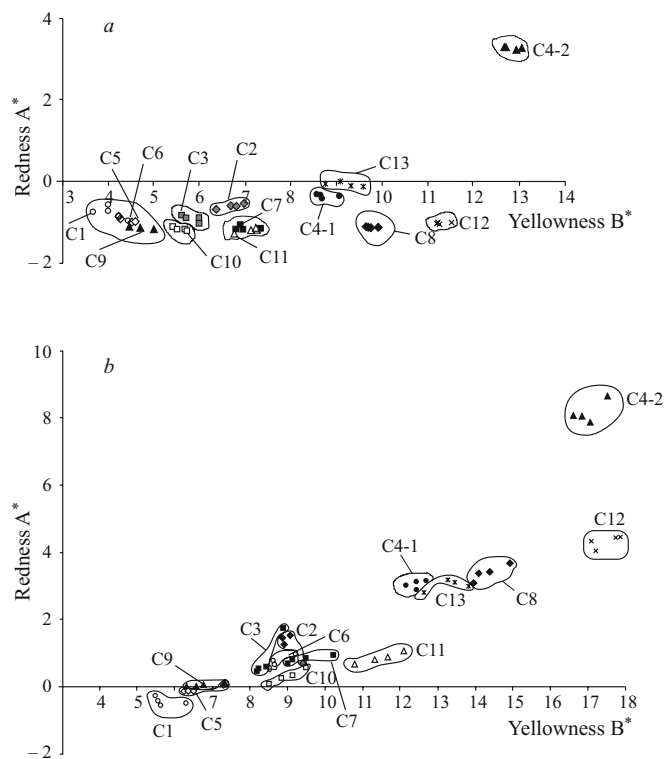
Fig. 1. Color coordinates $A^* - B^*$ of 14 samples of kaolin of 4 fractions (< 0.063, < 0.040, < 0.032, and < 0.020 mm) dried at 100°C (*a*) and heat-treated at 550°C (*b*).

must be based on a single indicator, which can easily characterize the color of an object even if a sample is not available.

This makes it necessary to classify kaolin according to color and whiteness indicators.

The objective of our work is to investigate the coloristic characteristics of kaolin and develop a method of multidimensional gradation of kaolin with respect to color indicators. This requires solving two basic problems:

determine the boundaries of the region in the MKO $L^*A^*B^*$ colorimetric system which correspond to the color of kaolin from the Zhuravlinyi Log deposit;

determine the relationship between the structural-mineral form of iron oxides in kaolin samples and their color indicators as a function of the heat-treatment conditions.

If the solution of the first problem makes it possible to construct a system of multidimensional gradation of kaolin according to the color indicators and to determine the whiteness intervals corresponding to different levels of competitiveness, then the solution of the second problem is simply identifying the latent (hidden) component of the coloring power of iron compounds in kaolin according to the color indicators.

Two hundred samples of enriched kaolin from the Zhuravlinyi Log deposit were investigated. These samples included 186 samples of raw kaolin obtained over the entire volume of the new sections of the deposit. Fourteen commercial-technological samples of enriched kaolin were prepared

from them (sample indices C1 – C13). The enrichment of the samples of raw kaolin was conducted under laboratory conditions on a No. 0063 sieve. Commercial – technological samples of kaolin were enriched through a system of sieves with separation into fractions < 0.063, < 0.040, < 0.032, and < 0.020 mm.

The kaolin samples differ with respect to the content of Fe_2O_3 (from 0.21 to 2.02%[2]) and TiO_2 (from 0.06 to 2.33%).

The kaolin samples were dried at temperature 100°C and heat treated in an electric furnace at 475, 550, 900, 1100, and 1250°C with a holding period of 10 min at the maximum temperature.

A "Pul'sar" spectrocolorimeter was used to perform measurements of the reflection spectra. The following parameters were used for performing measurements on samples with $d/8$ geometry: measurement neglecting the reflective component; color source — C, observer — MKO 1931, number of measurements — 3, interval between measurements — 5 sec. The standard radiation of the source C is the average daylight.

The MKO $L^*A^*B^*$ colorimetric system was used to study the effect of coloring impurities on the color of kaolin [5]. This system creates a numerically continuous color space, and it gives a quantitative representation of the contribution of the four basic colors in Cartesian coordinates. The abscissa characterizes the degree of redness ($+ A^*$) and greenness ($- A^*$); the ordinate characterizes the degree of yellowness ($+ B^*$) and blueness ($- B^*$). The point at the origin characterizes achromatic colors. The third axis, oriented perpendicular to the A^*B^* plane, determines the lightness L^*.

The color hue H was calculated using the relation

$$H = \arctan (B^*/A^*),$$

where A^* and B^* are the color coordinates of the sample.

The color difference between the samples was determined from the equation [5]

$$\Delta E = \sqrt{(L_1^* - L_2^*)^2 + (A_1^* - A_2^*)^2 + (B_1^* - B_2^*)^2}.$$

The whiteness of the kaolin samples was evaluated with the formula [5]

$$W_{ISO} = Y + 800(x_n - x) + 1700(y_n - y),$$

where Y is the color coordinate of the sample; x_n and y_n are the color coordinates of the achromatic point for the chosen observer (2°); x and y are the color coordinates of the sample.

The yellowness G was evaluated according to the ASTM D1925 standard procedure [5]:

$$G = ((1.28X - 1.06Z)/Y) \times 100,$$

where X, Y, and Z are the color coordinates of the sample.

The relative coloring power of the iron compounds in kaolin was evaluated by the procedure described in [6]. This

---

[2] Here and below — content by weight.

TABLE 1.

Sample	Color coordinates						Color difference $\Delta E\,(L^*A^*B^*)$
	after drying at 100°C			after heat-treatment at 550°C			
	L^*	A^*	B^*	L^*	A^*	B^*	
C1	95.38	− 0.63	3.68	92.29	− 0.26	5.48	3.51
C4-2	88.35	2.79	12.67	80.79	8.65	17.53	10.66
C5	95.19	− 0.85	4.53	92.29	0.06	7.29	4.13
3	88.92	− 0.09	9.32	83.20	3.01	13.83	9.90

procedure is based on determining the reflection spectrum of the control and experimental samples.

Figure 1*a* displays the values of the color coordinates of commercial-technological samples of kaolin from the Zhuravlinyi Log deposit, which were passed through a system of sieves and pre-dried at 100°C.

The kaolin samples C1 – C13 (with the exception of samples C4-2) lie on the yellowness line B^*. The C1, C5, and C9 samples have the lowest yellowness B^* and C4-2, C8 and C12, and C13 have the highest. In describing the kaolin samples it was found that they comprise three forms of kaolin with respect to their origin: C1, C2, C3, C4-1, C4-2 are kaolins in granite; C5 – C8 are alkaline kaolins in granite (with kaolin fraction > 50%); C9 – C12 are alkaline kaolins in granite (with kaolin fraction < 50%); C13 are kaolins in gneisses.

It should be noted that the content of iron oxides increases in each type of kaolin in the samples (from C1 to C13). Comparing the color coordinates with the content of coloring impurities, predominately iron oxides, it was found that the yellowness B^* of kaolin increases with the content of iron oxides: for $B^* = 3.68$ the content of iron oxides is 0.43% in sample C1, while for $B^* = 8.68$ it is 0.88% in sample C4-1; the samples C4-2 are exceptions — they are distinguished by high values of the yellowness ($B^* = 12.67 – 13.05$) and redness ($A^* = 2.74 – 2.80$). Therefore the red-yellow tinge of kaolin is due to the total content and structure-mineral form of iron.

The differences between the values of the color indicators of each sample of kaolin which has passed through the system of sieves (0.063, 0.040, 0.032, 0.20 mm) are negligible.

It was determined that the color difference $\Delta E\,(L^*A^*B^*)$ between the kaolin specimens from one sample with different fractions is negligible.

Thus, there is a very small color difference $\Delta E\,(L^*A^*B^*)$ between specimens which have passed through the indicated system of sieves. This shows that the effectiveness of the separation of kaolin into fractions is low.

Figure 1*b* displays the values of the color coordinates of kaolin samples with different fractions, which have passed through a system of sieves, after heat treatment at 550°C. It is evident that they fall essentially on a straight line with con-

stant increase of the redness A^* and yellowness B^* from the sample C1 to C12 (with the exception of sample C4-2) and a decrease of the values of the color hue from $H = 92$ (yellow-green) to $H = 77$ (red-yellow). The order of the arrangement of the kaolin samples remains essentially unchanged and is similar to their order in color coordinates (yellowness B^* – redness A^*) after drying at 100°C.

The color difference between the kaolin samples dried at 100°C and samples heat-treated at 550°C is substantial: $\Delta E\,(L^*A^*B^*)$ from 3 to 10 (Table 1). Apparently, the Zhuravlinyi Log kaolin deposit contains free iron compounds predominately in the structural and mineral forms with weak coloring power, which after heat-treatment transform into a mineral form with strong coloring power. Hematite is such a mineral.

The next problem of our investigation is to determine the coordinates of a color with the highest discrimination capability for color differences between kaolin samples as a function of their heat-treatment conditions.

Canonical discriminant analysis was used to solve this problem [7]. The calcination temperature of kaolin was taken as the classification variable. A number on the order scale was assigned to the kaolin samples heat-treated at the same temperature: group 1) samples dried at 100°C; 2) heat-treated at 475°C; 3) 550°C; 4) 900°C; 5) 1100°C; 6) 1250°C (Table 2).

Fisher's F test and Wilks' U test were used to check the significance of the canonical discrimination functions (CDF). Since the computed value of F (30.9) is substantially greater than the tabulated value of F (2.05), the statistical hy-

TABLE 2.

Group	Heat treatment, °C	Color coordinate		
		L^*	A^*	B^*
1	100	93.33	− 0.48	7.25
2	475	89.33	1.51	10.12
3	550	88.87	1.88	10.70
4	900	92.26	1.39	7.73
5	1100	94.86	− 0.27	4.19
6	1250	94.37	− 1.07	4.72
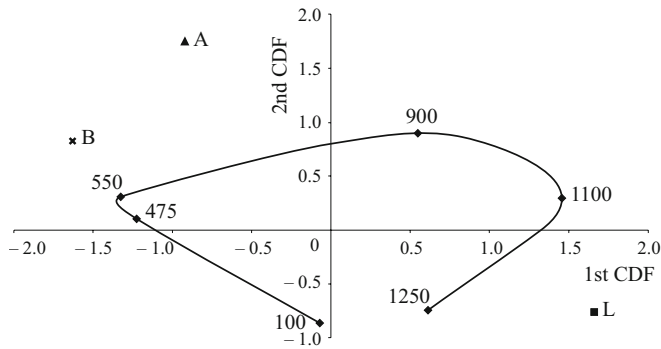
Fig. 2. Position of the centroid of the kaolin samples heat-treated at 100, 475, 550, 900, 1110, and 1250°C and the color coordinates in the plane of the coordinates of the 1st and 2nd CFD. Color coordinates: L^*) lightness, A^*) redness, B^*) yellowness.

pothesis of color indistinguishability between groups of kaolin samples as a function of their heat-treatment temperatures can be rejected at significance level $\alpha < 0.01$.

Now it is necessary to determine the contribution of discriminant variables to the difference between groups. The values of the F exclusion (Table 3) for the variables — color coordinates — are greater than the tabulated values of (3.11) at significance level $\alpha < 0.01$. Consequently, it can be stated that the three color coordinates are significant for separating kaolin samples into three groups depending on their heat-treatment temperatures. On the basis of the values of the F exclusion criterion the color coordinates of kaolin can be arranged as a function of the heat-treatment conditions according to their discriminating power in the following sequence: $F(A^*) \gg F(L^*) > F(B^*)$.

Therefore, the redness A^* of kaolin is a indicator which best discriminates kaolin samples as a function of their heat-treatment temperature; the lightness L^* and yellowness B^* are less effective. It is known [8] that the redness of kaolin is due to the main coloring iron compound — hematite. Synthesis and reverse processes of the transformation of hematite (destruction and dissolution) promote the formation of kaolin color depending on the heat-treatment conditions.

As expected, three characteristic values of the CDF, different from zero, were identified. They lie in order of decreasing magnitude. The characteristic value is related with the discriminating possibilities of this function: the larger the characteristic value, the better the kaolin samples separate into groups depending on the heat-treatment conditions: the 1st CDF possesses the greatest possibilities — 67.4% of the

total discrimination; the 2nd CDF — 25.5%; and, the 3rd CDF — 7.1%.

The statistical significance of the CDF was checked according to the residual discrimination power of Wilks' U test and according to the χ^2 test. It can be asserted that the 1st, 2nd, and 3rd CDF are statistically significant on the whole as a system for distinguishing the color of kaolin samples after they have been heat treated. But the small values of the cumulative fraction of the 3rd CDF and the values according to the residual discrimination power up to its identification close to 1 (Wilks' U factor equals 0.90) as well as its weak canonical correlation with groups show that the main color discrimination of kaolin as a function of its treatment temperature is described by two CDF (their cumulative fraction is 92.9%).

It is helpful to use the standardized coefficients to find the variables that make the largest contribution to the CDF. The absolute value of a coefficient is analyzed in the standard form: the larger the value, the greater the contribution of this variable is. For the 1st CDF all three variables — color coordinates — are significant when the lightness predominates L^*; for the 2nd CDF — two variables — the redness A^* and the yellowness B^* — with redness coordinate A^* predominating.

The structural coefficients, in contrast to the standardized coefficients, are used for informative interpretation of the functions. Table 4 gives the values of the structural coefficients. They show how closely related the variables — color coordinates — are to the two discriminant functions. On the basis of the signs and absolute value of the structural coefficients of the variables of the 1st CDF, it can be interpreted as the axis of the relation "lightness versus yellowness" and for the 2nd CDF as the "redness axis."

Examining the values of the group centroids in the coordinates of the 1st and 2nd CDF, the color differences between the kaolin samples can be interpreted as a function of the heat-treatment conditions (Fig. 2).

Three different intervals of color discrimination of kaolins as a function of the treatment temperature can be conditionally separated in the coordinates of the 1st and 2nd CDF: in the first one — from 100 to 475 – 550°C — the redness A^* and yellowness B^* increase while lightness L^* decreases substantially; in the second one — 550 – 1100°C — the lightness L^* increases and the redness A^* and yellowness B^* decrease; in the third one — 1100 – 1250°C — the redness A^* decreases.

TABLE 3.

Variable	Wilks' U test	F exclusion
L^*	0.41	18.27
A^*	0.48	33.43
B^*	0.39	13.42

TABLE 4.

Variable	1st CDF	2nd CDF
L^*	0.84	− 0.52
A^*	− 0.48	0.86
B^*	− 0.80	0.42
Cumulative fraction, %	67.4	25.5
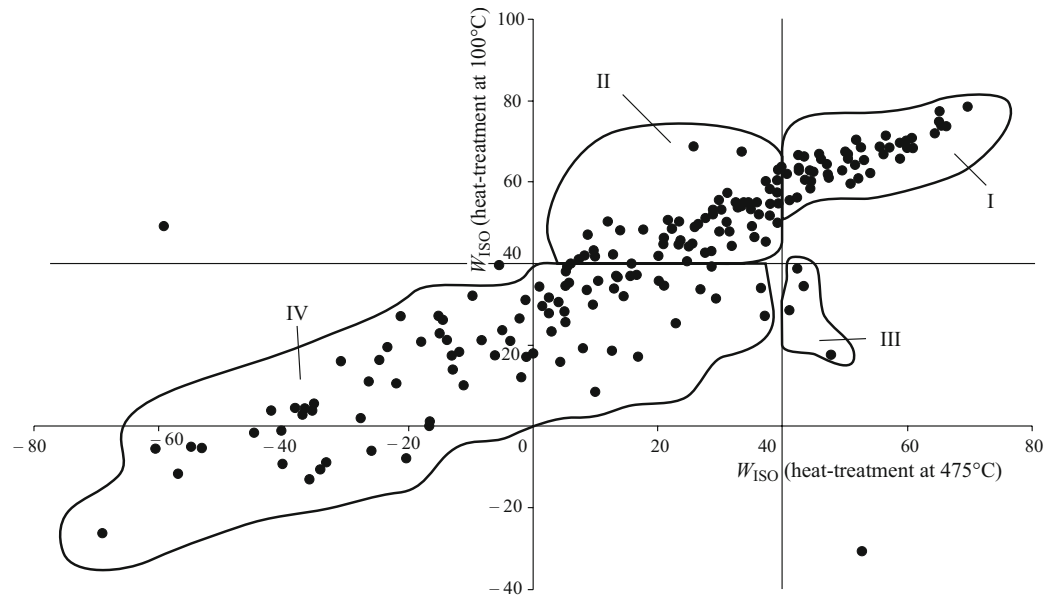
Fig. 3. Arrangement of points corresponding to whiteness W_{ISO} of kaolin samples heat-treated at 100 and 475°C. I – IV) groups of kaolin samples.

Thus, discriminant analysis makes possible, in the first place, an interpretation of the color formation processes in kaolin after it has undergone treatment at different temperatures; in the second place, it permits evaluating the contribution of the variables — color coordinates — to the dominant processes in each heat-treatment interval.

Comparing the arrangement of the centroids of groups corresponding to the average values of the coloristic characteristics of kaolin samples as a function of the heat-treatment conditions (see Table 2), in the coordinates of the 1st and 2nd CDF (see Fig. 2), with the values of the relative coloring power of iron compounds in kaolin as a function of the content of iron oxides and treatment temperature (Table 5) identifies to important features:

the maximum of the coloring power of the iron compounds in kaolin is observed after the kaolin has undergone heat-treatment at 475 – 550°C and the minimum is observed after drying at 100°C and heat-treatment at 1100 – 1250°C (see Table 5);

The centroids of groups corresponding to kaolin samples after drying at 100°C and after heat-treatment at 1250°C have the minimum separation from one another (see Fig. 2).

The main factors affecting the color of kaolin have been listed above. After the kaolin has undergone heat-treatment at temperature above 1100°C most of the iron passes into a magnetically dilute state whose coloring power is minimum. In addition, mullite crystals are formed during heat-treatment of kaolin. These crystals strongly scatter light and neutralize the coloring effect of the iron compounds. As a result, the whiteness and coloristic characteristics of the kaolin should not be measured after the kaolin has been heat-treated at temperatures above 1100°C.

It was determined that the iron compounds present in kaolin heat-treated at 475 – 550°C have the highest coloring power (see Table 5). Consequently, a multidimensional gra-

dation of kaolin samples according to their coloristic characteristics after drying and heat-treatment at 475°C was performed.

According to GOST R ISO 105-J02–99 materials for which the whiteness $W_{ISO} > 40$ are white (material for which $W_{ISO} < 40$ are not white). The kaolin samples heat-treated at 100 and 475°C were divided into groups in accordance with this norm (Fig. 3):

group I consists of kaolin samples whose whiteness $W_{ISO} > 40$ are heat-treatment at 100 and 475°C;

group II consists of samples with $W_{ISO} > 40$ after drying and < 40 after heat-treatment at 475°C;

group III consists of samples with $W_{ISO} < 40$ after drying and > 40 after heat treatment; and,

group IV consists of samples for which $W_{ISO} < 40$ after drying and heat-treatment at 475°C.

The samples I and II are of greatest interest. After drying and heat-treatment at 475°C the group-I samples possess whiteness which allows classifying them as white materials. After drying group-II samples are white, but after heat-treatment they are not white.

TABLE 5.

Treatment temperature, °C	Relative coloring power, %, of the sample		
	C1	C4-2	C13
100	100.0	100.0	100.0
475	223.4	199.8	243.0
550	257.3	249.2	283.4
900	106.5	134.9	159.2
1100	48.7	63.7	37.6
1250	97.0	80.2	27.5
Fe_2O_3 content, wt. %	0.45	1.39	1.75

TABLE 6.

Quality category	Treatment temperature, °C			
	100		475	
	W_{ISO}	G	W_{ISO}	G
1	> 70	< 7	> 56	< 10
2	66 – 70	7 – 10	46 – 56	10 – 15
3	55 – 65	10 – 16	37 – 45	15 – 20

Apparently, group-II kaolins contain iron compounds whose coloring power is low, and after heat treatment the coloring power is high, so that the whiteness of the kaolin decreases. Most of the iron compounds present in the kaolins belonging to this group are predominately in a structural-mineral form which exhibits weak coloring power. Consequently, these kaolin samples have a higher whiteness as compared with the analogous samples with the same or higher content of iron oxides. In this connection, a new terminology has been proposed — "latent (hidden) component of coloring power" of iron compounds when evaluating their effect on the color of kaolin.

In summary, a procedure has been proposed for identifying the latent (hidden) component of the coloring power of iron compounds in kaolin that is based on determining the gradient in whiteness coordinates W_{ISO} of kaolin samples heat-treated at 100 and 475°C and identifying the region in the white — not white coordinate plane ($W_{ISO} > 40$ – $W_{ISO} < 40$).

A multidimensional gradation of group-I kaolin samples according to whiteness W_{ISO} and yellowness G (ASTM) was performed according to quality categories (Table 6).

Kaolin from the first quality category can be used to produce high-quality premium-class porcelain; category-2 kaolin can be used for economical-grade porcelain; category-3 kaolin can be use for sanitary-technical ware porcelain, which is covered with a white opaque glaze.

REFERENCES

1. A. C. Scheinost and U. Schwertmann, "Color identification of iron oxides and hydroxysulfates: use and limitations," *Soil Sci. Soc. Am. J.*, **63**, 1463 – 1471 (1999).
2. Yu. N. Vodyanitskii, *Chemistry, Mineralogy, and Color of Gleyed Soils* [in Russian], Moscow (2006).
3. R. A. Khalilullova, *Increasing the Whiteness of Porcelain by Integrated Treatment of the Mineral Initial Materials, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (1994).
4. O. V. Glazkov, *Investigation of the Color Characteristics of Lay-Containing Materials and Porcelain Based on Them, Author's Abstract of Candidate's Thesis* [in Russian], Moscow (2005).
5. *Color in Industry* [in Russian], Logos, Moscow (2002).
6. *Handbook of Investigation Methods in Textile Chemistry* [in Russian], Moscow (1993).
7. D. O. Kim, Ch. U. Mueller, U. R. Klekka, et al., *Factor, Discriminant, and Cluster Analysis* [Russian translation], Finansy i Statistika, Moscow (1989).
8. G. N. Maslennikova, K. A. Kuvshinova, and Yu. T. Platov, "Structural – phase changes of iron-containing impurities in porcelain formation," *Steklo Keram.*, No. 12, 11 – 14 (1997).